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**EP 0200466 A US 4466486 A US 4436638 A**

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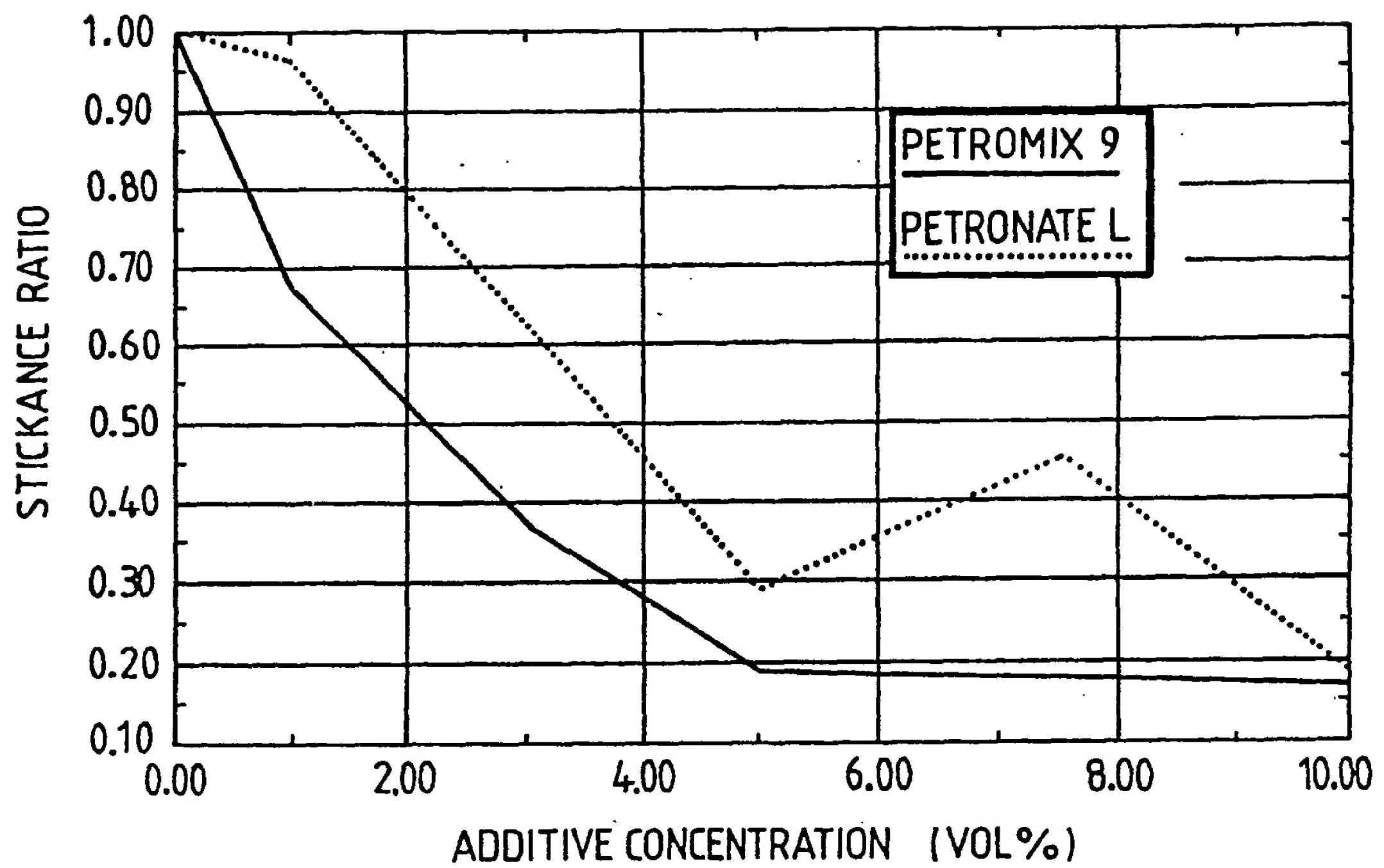
**INT CL<sup>5</sup> C09K, E21B**

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(54) **Additives for water-based drilling fluid**

(57) An additive for a water-based fluid which is to be used when the likelihood of differential sticking is high and which reduces the sticking tendency of the fluid and mud cake. An additive according to the invention comprises a well dispersed-particulate phase such as an emulsion, a fine emulsion, a microemulsion, a micellar phase or a polymeric phase having a particle size comparable with the pore throat size of a mud cake and comprising a material which forms easily deformable particles and which reduces the sticking propensity of the mud. One embodiment of the invention comprises a microemulsion of an oil which is well dispersed, substantially stable and has a substantial portion of the particle size distribution in the range 5 - 500 nm. An alternative embodiment comprises a micellar phase comprising one or more surfactants. The additive is typically used at a level of about 5% by volume in the drilling fluid.

GB 2 277 759 A



*Fig. 1*

## ADDITIVES FOR WATER-BASED DRILLING FLUID

The present invention relates to a series of additives for use in water-based drilling fluids which can reduce the likelihood of differential sticking of drill pipe, logging tools or coiled tubing when drilling oil or gas wells or the like.

In the rotary drilling of oil or gas wells, a drilling fluid is used which is pumped down into the well inside the drill string and returns to the surface via the annulus formed by the outside of the drill string and the well bore. The drilling fluid typically comprises a liquid carrier, usually water (or brine) but sometimes oil, a viscosifier which is often bentonite clay, a weighting agent such as barite, and a number of additives for modifying the properties of the fluid. As the drilling takes place, a certain amount of liquid phase can sometimes permeate into the drilled rock causing the solids to be filtered at the borehole wall so as to form a filter cake or mud cake. The mud cake prevents further fluid loss to some degree. However, if the mud cake continues to grow there is a danger of differential sticking of the drill pipe. Differential sticking occurs when the mud cake of a water-based fluid grows so as to contact the drill pipe and will typically occur when the pipe is not rotating or otherwise moving (this happens to a much less degree with oil-based fluids). The pipe sticks when the torque or overpull which is available is insufficient to free the pipe from the mud cake. Various additives have been proposed to assist in freeing stuck drill pipe, the most common of which is diesel oil which is added directly to the drilling mud as a "spotting fluid". However this is not always successful.

It is an object of the present invention to provide an additive for a water-based fluid which is to be used when the likelihood of differential sticking is high and which reduces the sticking tendency of the fluid and mud cake.

An additive according to the present invention comprises a well dispersed particulate phase having a substantial portion of the particle size comparable with the pore throat size of a mud cake and being deformable so as to provide little effective resistance to an applied shear stress.

It is preferred that the particulate phase has a relatively broad particle size distribution so as to correspond to the distribution of pore throat size in the mud cake. The invention typically comprises an emulsion such as a fine emulsion, or a microemulsion or a micellar phase having a substantial portion of the particle size distribution in the range 5-500 nm. One embodiment of the invention comprises an oil-in-water microemulsion.

In an alternative embodiment, the additive comprises a micellar phase comprising one or more surfactants.

In a further alternative embodiment, the additive comprises a polymeric material, such as a soft microgel or high molecular weight individual molecules.

A typical additive comprising an oil-in-water microemulsion might comprise 40% by volume oil and 60% by volume surfactant. The oil may be a single oil or a mixture of different oils. The oils can be mineral, animal or vegetable oils. The surfactant can be anionic, cationic or non-ionic, anionic surfactants such as sulphonates being preferred. Secondary, surfactants or cosurfactants such as ethylene glycol or diethylene glycol can be used and an ionic surfactant such as the sodium salt of dodecyl benzene sulphonic acid can be used. An additive of this type might be used at a level of about 5% by volume in the water-based drilling fluid. The resultant emulsion might have the following properties:

- the emulsion structures are formed on a smaller length scale than traditional polymeric fluid loss control agents, so as to block pores in the mud cake decreasing fluid loss and cake growth.
- the surfactant adsorbs preferentially onto the surfaces of clay or other minerals such as barite so as to allow more efficient packing and so less permeable cakes which inhibit fluid loss and cake growth.
- the dispersed phase remains in the cake and becomes a fluid part of its structure, thus reducing the yield strength of the cake.
- excess surfactant, the emulsion structures or both may lubricate the interface between the pipe and the mud cake.

When the additive comprises a micellar phase, it is preferred that an anionic surfactant is used although nonionic and cationic surfactants might also be suitable. Typically, the surfactant is a salt of dodecyl benzene sulphonic acid. This is usually the isopropylamine salt although the potassium or calcium salts may also be used. A mixture of surfactants can be used to provide a micellar phase such as mixtures of anionic and nonionic surfactants eg sodium and isopropylamine salts of dodecyl benzene sulphonic acid with coconut diethanolamide. The surfactants forming the micellar phase are typically present at a level of about 5% by volume in the water-based drilling fluid.

A water-based drilling fluid incorporating the micellar phase additive might have the following composition:

<b>Component</b>	
anionic surfactant	} 5% volume total
co-surfactant (optional)	
inorganic salt	4-6 g l <sup>-1</sup>
bentonite clay	40-80 g l <sup>-1</sup>
fluid loss control polymer, eg CMC	3 g l <sup>-1</sup>
antifoaming agent	<1 g l <sup>-1</sup>
weighting agent	as required

The various aspects of the present invention will now be described with reference to illustrative examples and to the accompanying drawing which shows a plot of the variation in stickance ratio with additive concentration.

In the following examples, the performance of the various additives is assessed by two main tests. The differential sticking propensity (hereinafter "stickance") is the scaled rate of increase of torque required to initiate rotation of a spherical body after a mud cake has formed. The device used to measure this property and the general method used is described in British Patent Application No. 9303321.5. In the present case, performance data is derived by comparing the performances of a water-based fluid comprising 20% volume barite, CMC, salt, polymeric thinner and a biocide, with and without the relevant additive, the results being expressed as a ratio. An additive which provides a ratio of 1 has no effect while a ratio of 0 indicates that the sticking tendency has been eliminated completely.

#### Example 1

The additive in this case is either Petromix 9, a blend of petroleum sulphonates, cosurfactants and oil, or Petronate L surfactant and oil blend which forms a microemulsion or fine emulsion when added to the mud. Figure 1 shows the variation of stickance ratio with additive concentration for both Petromix 9 and Petronate L in the general mud formulation given above. 5% by volume appears to be the optimum level with little extra benefit being obtained above this level.

Petromix 9 is sold as an oil-soluble emulsifier for use as a soluble cutting oil, textile processing oil or metal degreaser and Petronate L as a surfactant. Both are available from Witco BV, Worcester, UK.

#### Example 2

The effect of different surfactant to oil ratio is shown in Figure 2. In this case, the (micro) emulsion is formed from IDBS and PLANTOHYD oil in the mud. Little reduction in sticking is seen with 5% volume oil alone but as the proportion of surfactant increases the stickance decreases. The mean particle size of the emulsion

also decreased with increasing surfactant concentration although addition of IDBS above 60% volume leads to detrimental gelling of the mud.

### Example 3

(Micro) emulsion additives are created by mixing anionic surfactant, IDBS, and various oils in a ratio of 3:2 (by volume). These mixtures are then added to the standard mud described above at 5% by volume level and stickance tests performed. The results of these tests are given in Table 1 below. The fluid loss figures relate to a 30 minute loss test from a HPHT filtration cell at 200 psi differential pressure.

Table 1

<i>Oil</i>	<i>Stickance Ratio</i>	<i>Fluid loss (ml)</i>
Plantohyd	0.34	1.5
Fish	0.32	1.4
Corn	0.33	1.4
Peanut	0.38	1.2
Safflower	0.43	1.4
Shellsol	0.48	1.0

### Example 4

Further examples of (micro) emulsion additives were created by mixing various surfactants with a mineral oil and the mixtures were added to the standard mud and stickance ratio and fluid loss measured as before. The various surfactants and surfactant/oil ratios are given in Table 2 below together with the test data. It is to be noted that anionic surfactants are superior to nonionic or cationic surfactants in providing the required property without affecting mud rheology. Sulphonates appear to be the best anionic surfactants.

It is to be noted that Petromix 9 already includes oil and the Petronates are listed in ascending order of molecular weight.

Table 2

Tradename	Composition	Surfactant /oil ratio	Stickance ratio	Fluid loss (mL)
-	Standard WBM	-	1.0	3.2
-	Standard WBM +oil	-	0.9	2.2
<b>Standard WBM + Additive (Anionic surfactant)</b>				
Petromix 9	Petroleum sulphonate blend	3:2	0.2	0.4
Petronate L	Petroleum sulphonate	3:2	0.31	1.3
Petronate HL	Petroleum sulphonate	3:2	0.43	1.0
Petronate H	Petroleum sulphonate	3:2	0.36	1.6
Petronate HH	Petroleum sulphonate	3:2	0.26	1.4
Roval IDBS	IDBS	3:2	0.63	1.4
Sulframin 1250	NaDBS	3:1	0.71	1.8
-	KDBS	3:2	0.55	1.9
Sulframin AOS	Sodium dodecyl sulphonate	2:3	0.73	2.0
ROVAL 70PG	Diocetyl sulphosuccinate	3:2	0.57	1.5
EMPHOS 20 PS21A	Organic phosphate ester	2:3	1.81	13.5
TWEEN 20	Polyoxyethylene sorbitan monolaurate	3:2	1.46	6.2
<b>Standard WBM + Additive (Nonionic surfactant)</b>				
Synperonic 91/4	Alkyl phenol ethoxylate	3:2	0.29	7.0
Rewo RO 40	Ethoxylated caster oil	3:2	2.9	9.2
<b>Standard WBM + Additive (Cationic surfactant)</b>				
Ethoxamine SF11	Ethoxylated fatty amine	3:2	0.71	3.3
Sochamine 35	Imidazoline	3:2	0.56	8.2

Example 5

Cosurfactants can be used to enhance and extend the performance of microemulsion additives by modifying the droplet size over the range of operating conditions used. The cosurfactants are characterised in that they produce no reduction in sticking when used on their own but provide an improvement when added to a surfactant/oil mixture. Table 3 below summarises the effect of various cosurfactants with regard to the performance of a standard WBM including Petronate L as an additive.



**Table 3**

<i>Cosurfactant</i>	<i>% by volume of Petronate L in mud</i>	<i>Stickance Ratio</i>	<i>Fluid Loss (ml)</i>
-	5.0 (no oil)	0.31	1.4
-	3.0 (no oil)	0.65	1.4
-	3.0	0.41	1.2
Ethylene glycol	2.5	0.30	0.9
Diethylene glycol	2.5	0.33	1.3
Soft soap	3.0	0.41	0.9
Soft soap/Ethylene glycol	2.5	0.35	1.2
Sulframin AOS	3.0	0.38	0.9
Sulframin AOS/Ethylene glycol	2.5	0.36	1.3

In Table 3, the soft soap used is the potassium salt of a long chain carboxylic acid and Sulframin AOS is the sodium salt of dodecyl benzene sulphonic acid (an anionic surfactant). Sulframin AOS differs from the other cosurfactants in that it will produce a reduction in sticking when used on its own.

#### Example 6

In order to form a micellar phase additive it is necessary for the surfactant used to be added to the mix-water used to make up the mud. If the surfactant is added directly to the mud it may interfere with the clay-clay interactions and cause gelling. Table 4 below shows the performance of various additives formed from the isopropylamine (IDBS) or other salts of dodecyl benzene sulphonic acid. In each case the mud contains surfactant at 5% by volume.

**Table 4**

<i>Surfactant</i>	<i>Stickance Ratio</i>	<i>Fluid Loss (ml)</i>
IDBS	0.19	1.1
NaDBS	0.90	3.0
KDBS	0.22	1.3
CaDBS	0.39	1.6



### Example 7

Even when the surfactant is mixed with water prior to mixing into the mud, some effect can be seen on the rheology of the resulting mud. This can be controlled with traditional additives as can be seen in Table 5 below.

Table 5

<i>Composition</i>	<i>Plastic Viscosity (cP)</i>	<i>Yield Point (Pa)</i>
Base mud	66	48
Base mud + 5% IDBS	60	72
Base mud, 5% IDBS + 0.15% thinner	53	54

### Example 8

Combination of surfactants such as anionic and nonionic surfactants can be used to provide the desired effect. A suitable mixture might comprise sodium and isopropylamine salts of dodecyl benzene sulphonic acid with coconut diethanolamide.

## CLAIMS

- 1 An additive for a water-based drilling fluid comprising a well dispersed particulate phase having a substantial portion of the particle size comparable with the pore throat size of a mud cake and being deformable so as to provide little effective resistance to an applied shear stress so as to reduce the sticking propensity of the mud.
- 2 An additive as claimed in claim 1, wherein the particulate phase has a particle size distribution which corresponds substantially to the pore throat size distribution of the mud cake.
- 3 An additive as claimed in claim 1 or 2, wherein the particulate phase comprises an emulsion, a microemulsion, a micellar phase or a polymeric phase.
- 4 An additive as claimed in claim 1, 2 or 3, comprising a particulate phase which is well dispersed, substantially stable and has a substantial portion of the particle size distribution in the range 5-500 nm.
- 5 An additive as claimed in claim 1, 3 or 4, wherein the particulate phase in the drilling fluid comprises an oil-in-water fine emulsion or microemulsion.
- 6 An additive as claimed in claim 5, comprising about 40% by volume oil and about 60% by volume surfactant.
- 7 An additive as claimed in claim 5 or 6, wherein the oil comprises a mixture of oils.
- 8 An additive as claimed in claim 6, wherein the surfactant comprises one or more anionic, cationic or non-ionic surfactants.
- 9 An additive as claimed in claim 8, comprising at least one sulphonate surfactant.
- 10 An additive as claimed in any of claims 6, 8 or 9, further comprising at least one secondary or co-surfactant.
- 11 An additive as claimed in claim 3 or 4, comprising a micellar phase comprising one or more surfactants.

- 12 An additive as claimed in claims 11, comprising at least one anionic, cationic or non-ionic surfactant.
- 13 An additive as claimed in claim 11 or 12, wherein the micellar phase comprises a salt of dodecyl benzene sulphonic acid.
- 14 An additive as claimed in any of claims 11, 12 or 13, wherein the micellar phase comprises a mixture of surfactants
- 15 An additive as claimed in claim 14, wherein the micellar phase comprises a mixture of a salt of dodecyl benzene sulphonate and coconut diethanolamide.
- 16 An additive as claimed in claim 3 or 4, wherein the additive comprises a polymeric phase.
- 17 An additive as claimed in claim 16, wherein the polymeric phase comprises a soft microgel or high molecular weight individual molecules.
- 18 A water based drilling fluid comprising an additive as claimed in any preceding claim.
- 19 A water based drilling fluid as claimed in claim 18, wherein the additive is present in an amount of about 5% by volume.

**Amendments to the claims have been filed as follows**

- 1 An additive composition for a water-based drilling fluid, the composition comprising an aqueous dispersion of a particulate phase a substantial portion of the particles of which have a size comparable with the pore throat size of a mud cake, the particulate phase being in the form of an emulsion, a microemulsion or a micellar phase, and being deformable so as to provide little effective resistance to an applied shear stress so as to reduce the sticking propensity of the mud.
- 2 An additive as claimed in claim 1, wherein the particulate phase has a particle size distribution which corresponds substantially to the pore throat size distribution of the mud cake.
- 3 An additive as claimed in claim 1 or 2, wherein the particulate phase has for the substantial portion a particle size distribution in the range 5-500 nm.
- 4 An additive as claimed in any of claims 1 to 3, wherein the particulate phase exists in the form of an oil-in-water fine emulsion or microemulsion, with about 40% by volume oil and about 60% by volume surfactant.
- 5 An additive as claimed in claim 4, wherein the oil comprises a mixture of oils.
- 6 An additive as claimed in either claim 4 or 5, including at least one sulphonate surfactant.
- 7 An additive as claimed in any of claims 4 to 6, further including at least one secondary or co-surfactant.
- 8 An additive as claimed in any of claims 1 to 3, wherein the particulate phase comprises a micellar phase of one or more surfactants.
- 9 An additive as claimed in claim 8, wherein the micellar phase includes a salt of dodecyl benzene sulphonic acid.
- 10 An additive as claimed in claim 9, wherein the micellar phase further includes coconut diethanolamide.

- 11 An additive as claimed in any of claims 1 to 10 and substantially as described hereinbefore.
- 12 A water-based drilling fluid including an additive as claimed in any preceding claim in an amount of about 5% by volume.
- 13 A water-based drilling fluid as claimed in claim 11 or 12 and substantially as described hereinbefore.
- 14 A method of preventing the caking of drilling mud in a well, and thus reducing the likelihood of differential pipe sticking, in which method there is used a water-based drilling fluid as defined in either of claims 12 and 13.
- 15 A method as claimed in claim 14 and substantially as described hereinbefore.

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 Examiner's report to the Comptroller under  
 Section 17 (The Search Report) -12-

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**Relevant Technical fields**

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**Databases (see over)**

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

**Date of Search**

14 JUNE 1993

Documents considered relevant following a search in respect of claims

1-19

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0200466 A (TEXACO)	1-10, 18 19
X	US 4466486 (WALKER)	1-4, 16-19
X	US 4436638 (WALKER)	1-10, 18, 19

Category	Identity of document and relevant passages -13-	Relevant claim(s)

### Categories of documents

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